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Platinum Complexes with Optical Limiting and Related Non-linear Optical and Electronic Properties

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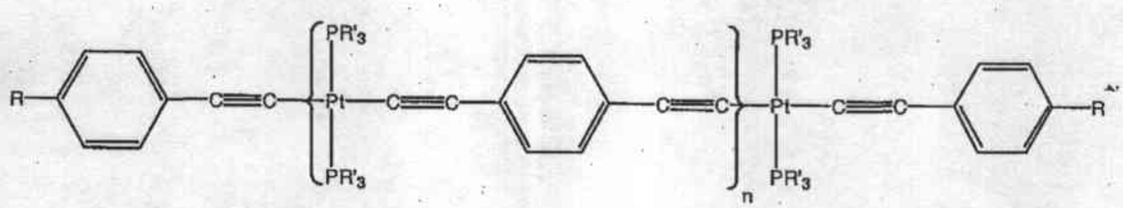
Introduction

This program consisted of applying several synthetic approaches, some derived from model studies of molecular wires, to the production of several novel types of platinum-alkynyl complex. In these, various components of the "platinum-ethynyl" model complexes **A** (n = 1, 2) will be modified in stepwise fashion.



(A) n = 1, 2

In addition to the relatively small alterations in properties achieved by changes in the ligands attached to the metal centre(s), significant modifications of the metal fragments responsible for (i) interaction with the unsaturated organic ligand (alkyne) and (ii) transfer of electronic properties between the ends of the molecule, are proposed. In this way, direct measurements of changes in the S° and T^{1} states were to be achieved.

Results

This project was developed according to the original proposal, progress being achieved in the individual stages outlined below.

(a) Syntheses of aromatic diynes, $RC{\equiv}CC_6H_4C{\equiv}CH$

Two routes were applied to the synthesis of these materials:

$$Me_3SiC{\equiv}CC_6H_4C{\equiv}CSiMe_3 + I\text{-}R \rightarrow RC{\equiv}CC_6H_4C{\equiv}CSiMe_3 + KF \rightarrow RC{\equiv}CC_6H_4C{\equiv}CH$$

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14. ABSTRACT
This project consisted of applying several synthetic approaches, some derived from model studies of molecular wires, to the production of several novel types of platinum-alkynyl complexes.

15. SUBJECT TERMS

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(R = Ph, 4-$MeOC_6H_4$, 4-$NO_2C_6H_4$; groups chosen as electron-donating or electron-withdrawing examples)

$RC{\equiv}CH + IC_6H_4I \rightarrow RC{\equiv}CC_6H_4I + HC{\equiv}CSiMe_3 \rightarrow RC{\equiv}CC_6H_4C{\equiv}CSiMe_3 + KF \rightarrow RCCC_6H_4CCH$

In general, these are Sonogashira reactions which are carried out under the normal conditions.

The following compounds were obtained:

$PhC{\equiv}CC_6H_4C{\equiv}CSiMe_3$
$PhC{\equiv}CC_6H_4C{\equiv}CH$

(b) Syntheses of platinum complexes

Some of the aromatic diynes synthesised in (a) were coupled to platinum centres to give four types of complex:

trans-$PtCl_2(PBu_3)_2$ + $HC{\equiv}CC_6H_4C{\equiv}CR$ → *trans*-$ClPt(PBu_3)_2C{\equiv}CC_6H_4C{\equiv}R$ or *trans*-$Pt(C{\equiv}CC_6H_4C{\equiv}CR)_2(PBu_3)_2$, according to stoichiometry

trans-$ClPt(PBu_3)_2C{\equiv}CC_6H_4C{\equiv}CPtCl(PBu_3)_2$ + $HC{\equiv}CC_6H_4C{\equiv}CR$ → *trans*-$RC{\equiv}CC_6H_4C{\equiv}CPt(PBu_3)_2C{\equiv}CC_6H_4C{\equiv}CPtCl(PBu_3)_2$ or *trans*-$RC{\equiv}CC_6H_4C{\equiv}CPt(PBu_3)_2C{\equiv}CC_6H_4C{\equiv}CPtC{\equiv}CC_6H_4C{\equiv}CR(PBu_3)_2$, according to stoichiometry

Unsymmetrical compounds, in this case capped with a phenyl group, could be prepared from $PtClPh(PBu_3)_2$, itself obtained from the dichloro complex with $HgPh_2$.

The following complexes have been made and fully characterised:

Ph-$Pt(PBu_3)_2$-$C{\equiv}CPh$
Ph-$Pt(PBu_3)_2$-$C{\equiv}CC_6H_4C{\equiv}CPh$
Ph-$Pt(PBu_3)_2$-$C{\equiv}CC_6H_4C{\equiv}C$-$Pt(PBu_3)_2$-Ph

The effect of introducing a highly electron-withdrawing phosphine, namely tris(pyrrolidinyl)phosphine, $P(pyr)_3$, was investigated with the following complexes:

$PhC{\equiv}C$-$Pt\{P(pyr)_3\}_2$-$C{\equiv}CPh$
$PhC{\equiv}CC_6H_4C{\equiv}C$-$Pt\{P(pyr)_3\}_2$-$C{\equiv}CC_6H_4C{\equiv}CPh$

(c) Syntheses of aromatic 1,3-diynes and their platinum complexes

An alternative route to aromatic 1,3-diynes was developed, whereby extension of the carbon chain by a further C≡C triple bond can be achieved. As in (b), selected platinum complexes were made using these diynes as precursors:

$PhC{\equiv}CAu(PPh_3)$ + $IC{\equiv}CC_6H_4C{\equiv}CI$ → $PhC{\equiv}CC{\equiv}CC_6H_4C{\equiv}CH$ + *trans*-$PtCl_2(PBu_3)_2$ → *trans*-$PhC{\equiv}CC{\equiv}CC_6H_4C{\equiv}CPtCl(PBu_3)_2$ or *trans*-$Pt(C{\equiv}CC{\equiv}CC_6H_4C{\equiv}CPh)_2(PBu_3)_2$, according to stoichiometry

Synthesis and complete characterisation of *trans*-$Pt(C{\equiv}CC{\equiv}CC_6H_4C{\equiv}CPh)_2(PBu_3)_2$ is not yet complete.

(d) Complexes containing Pt_2 centres

In an effort to improve the interaction between the metal centre and the alkynyl group(s), diplatinum complexes containing some of the same alkynes and 1,3-diynes as described in (a) and (c) will be prepared. This was achieved by reactions of the dichloro-diplatinum complex $Pt_2Cl_2(\mu\text{-dppm})_2$ with the alkyne in the presence of sodium methoxide:

$Pt_2(\mu\text{-dppm})_2Cl_2$ + $2HC{\equiv}CR$ → $Pt_2(\mu\text{-dppm})_2(C{\equiv}CR)_2$

Using this route, the following compounds were prepared:

$PhC{\equiv}C\text{-}Pt_2(\mu\text{-dppm})_2\text{-}C{\equiv}CPh$
$HC{\equiv}CC_6H_4C{\equiv}C\text{-}Pt_2(\mu\text{-dppm})_2\text{-}C{\equiv}CC_6H_4C{\equiv}CH$
$PhC{\equiv}CC_6H_4C{\equiv}C\text{-}Pt_2(\mu\text{-dppm})_2\text{-}C{\equiv}CC_6H_4C{\equiv}CPh$

The presence of the strong base resulted in desilylation of trimethylsilylalkynes to produce the terminal alkynyl complexes

$HC{\equiv}C\text{-}Pt_2(\mu\text{-dppm})_2\text{-}C{\equiv}CH$
$HC{\equiv}CC_6H_4C{\equiv}C\text{-}Pt_2(\mu\text{-dppm})_2\text{-}C{\equiv}CC_6H_4C{\equiv}CH$

In the course of this work, it was found that the triflate group ($CF_3SO_3^-$, OTf^-) is a better leaving group, so that the silylated alkynyl derivatives were prepared from

$Pt_2(\mu\text{-dppm})_2(OTf)_2$ + $HC{\equiv}CC_6H_4C{\equiv}CR$ → $RC{\equiv}CC_6H_4C{\equiv}CPt_2(\mu\text{-dppm})_2C{\equiv}CC_6H_4C{\equiv}CR$

This route allowed preparation of the following derivatives:

$Me_3SiC{\equiv}C\text{-}Pt_2(\mu\text{-dppm})_2\text{-}C{\equiv}CSiMe_3$
$Me_3SiC{\equiv}CC{\equiv}C\text{-}Pt_2(\mu\text{-dppm})_2\text{-}C{\equiv}CC{\equiv}CSiMe_3$

Examples of complexes containing two platinum centres linked only by the bridging diphosphine ligands were also prepared by using lithiated alkynes:

$\{(PhC{\equiv}C)_2Pt(\mu\text{-dppm})\}_2$
$\{PhC{\equiv}CC_6H_4C{\equiv}C\}_2Pt(\mu\text{-dppm})\}_2$

(e) Introduction of redox-active metal fragments

Addition of redox-active fragments, particularly those based on the Ru(PP)Cp (PP = tertiary phosphine, to the mono- and diplatinum centres mentioned above, afforded complexes containing two carbon chains linked through the Pt or Pt_2 centres.

$Pt_2(\mu\text{-dppm})_2Cl_2$ + $Ru(C{\equiv}CSiMe_3)(dppe)Cp$ + KF $\rightarrow$ $Cp(dppe)RuC{\equiv}C\text{-}Pt_2(\mu\text{-dppm})_2\text{-}C{\equiv}CRu(dppe)Cp$

The following new complexes have been obtained by this route:

$Cp(Ph_3P)_2RuC{\equiv}C\text{-}Pt_2(\mu\text{-dppm})_2\text{-}C{\equiv}CRu(PPh_3)_2Cp$
$Cp(dppe)RuC{\equiv}C\text{-}Pt_2(\mu\text{-dppm})_2\text{-}C{\equiv}CRu(dppe)Cp$
$Cp(Ph_3P)_2RuC{\equiv}CC_6H_4C{\equiv}C\text{-}Pt_2(\mu\text{-dppm})_2\text{-}C{\equiv}CC_6H_4C{\equiv}CRu(PPh_3)_2Cp$
$Cp(dppe)RuC{\equiv}CC_6H_4C{\equiv}C\text{-}Pt_2(\mu\text{-dppm})_2\text{-}C{\equiv}CC_6H_4C{\equiv}CRu(dppe)Cp$

As suggested earlier in our original proposal and shown here by cyclic voltammetric studies, improved communication between the redox-active centres occurs in these complexes, in complete contrast to mono-platinum analogues, where the platinum atom acts as an insulator. These may allow better electron transfer to and from the alkynyl-platinum centres, leading to more ready access to the triplet state.

Complexes containing the more basic $\eta\text{-}C_5Me_5$ (Cp*) group are currently being investigated in the expectation that more efficient communication between the ruthenium centres will be evidenced.

(f) Modification of the carbon chain

Part (c) above will result in the preparation of compounds containing more than one C≡C triple bond in the chain. In principle, attachment of the C≡C triple bond to other metal fragments, such as $Co_2(CO)_6$, $Co_2(\mu\text{-dppm})(CO)_4$ or $Ru_3(CO)_{10}$, is possible and a few experiments have been carried out to determine the necessary reaction conditions.

The complex $PhC_2[Co_2(\mu\text{-dppm})(CO)_4]C_6H_4C{\equiv}C\text{-}Pt_2(\mu\text{-dppm})_2\text{-}C{\equiv}CC_6H_4C_2Ph[Co_2(\mu\text{-}dppm)(CO)_4]$ has been prepared and crystallographically characterised.

(g) Introduction of photo-active metal fragments

Improvements in performance may be achieved by combination of the optical-limiting fragment (platinum complex) with a photo-active fragment, e.g. the *rhenium-containing*

group illustrated below. However, lack of time precluded development of this part of the project.

(h) Oxidative coupling

Extension of the unsaturated carbon chain by oxidative coupling (Glaser, Eglinton or Hay conditions) will be attempted with appropriate complexes containing -CCH or -$CCSiMe_3$ groups. Again, lack of time precluded any studies of these reactions.

The new compounds obtained by the reactions summarised above have been characterised by elemental analyses and the usual spectroscopic methods (IR, UV-vis, NMR, MS) where applicable and, in two cases, by single-crystal X-ray structural determinations.

NLO studies

The NLO (optical limiting) properties of these materials were to have been measured in conjunction with Dr Peter Veitch, Department of Physics, University of Adelaide. During 2005, the nanoscecond laser required for these studies has been moved to another laboratory and was out of commission for the period of this preliminary study. Alternative arrangements are being sought with the Laser Hardened Materials Group (MLPJ/E) at Wright-Patterson AFB, Dayton, OH, and several of the compounds obtained during the work described above have been sent for measurements to be made. At the time of writing this report (December 2005), only ground-state UV-vis spectra have been obtained.

Personnel

Dr Benjamin Hall (Ph.D., Adelaide) returned from a three-year period spent at Wright-Patterson AFB, Dayton, OH, at the time this grant was awarded. Hall was then appointed as a Research Officer for a period of 30 weeks, his previous experience and skills in this type of work allowing a rapid development of the synthetic chemistry as described above. Although the final objectives have not been attained, his experience and contacts are appropriate for an understanding of the requirement for testing of these compounds at W-P AFB during next year.